

Announcements

47 people in recitation yesterday. Expect quizzes there and in class.

Chapter 6 Problems: 6.9, 6.11, 6.13(except c), 6.19, 6.23, 6.34, 6.38, 6.42, 6.51, 6.53, 6.54, 6.57, 6.64, 6.66, 6.69, 6.75, 6.78

Chapter 7 Problems 7.1, 7.2, 7.8, 7.12, 7.40, 7.48, 7.50, 7.51, 7.55 ,7.56, 7.60

Exam 3

Wednesday, September 30

CTC 6PM-7:30PM

Chapter 6-Chapter 11

Chapter 6: Thermochemistry

6.1 Forms of Energy and Their Interconversion

6.2 Enthalpy: Heats of Reaction and Chemical Change

Exam 2 up to and including p.234

6.3 Calorimetry: Laboratory Measurement of Heats of Reaction

6.4 Stoichiometry of Thermochemical Equations

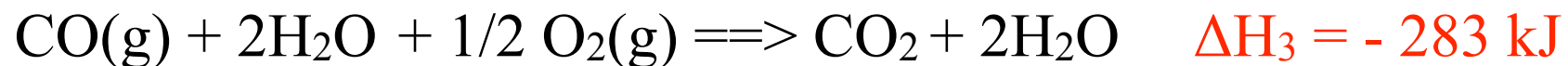
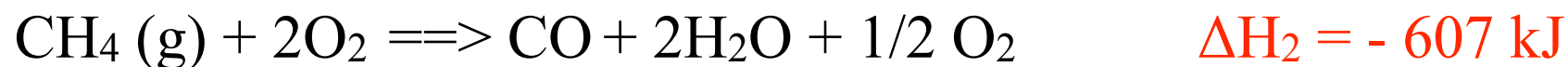
6.5 Hess's Law of Heat Summation

6.6 Standard Heats of Reaction (ΔH^0_{rxn})

- **Hess's Law:** The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for any individual step in the reaction. The heat of reaction for any reaction is a constant and depends only on the initial and final states (state function).

Suppose we want to know or find out the enthalpy for an unknown and can not measure it directly. Thermodynamics let's us calculate it.

Data From
A
Table



Physicists and chemists have defined a standard **thermodynamic “standard state”** (which is not the same as STP in gases) and denote with a superscript degree sign, ΔH°

Thermodynamic Standard State Conditions

- 1 atmosphere pressure
- $25^\circ\text{C} = 298.15\text{K}$
- 1 Molar concentration for solutions containing solutes



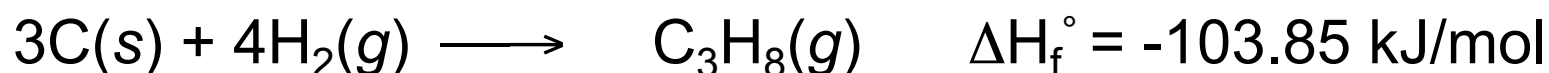
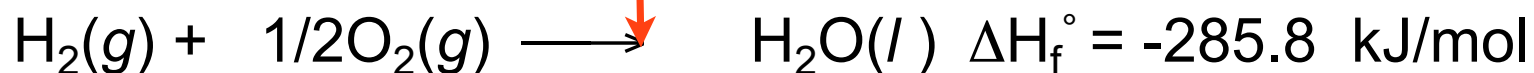
Conditions of P, T, [] are given in problem and stated

The superscript indicates thermodynamic standard state:
P = 1 atm, T = 298, [1M]

The **Standard Enthalpy of Formation, ΔH_f°** , is the enthalpy change associated with the formation of 1 mole of product **from its naturally occurring elements** under standard state conditions.

Note: 1 mol product!

•Examples:



Note: fractional coefficients allowed

- Oxygen exists as O_2 gas at 25°C
- Carbon exists as solid graphite (C) at 25°C .
- Sulfur exists as S_8 as a solid at 25°C
- Water is $\text{H}_2\text{O}(l)$ in its standard state (not ice or water vapor).

It is also not possible to measure the “absolute enthalpy”. We define an arbitrary scale with the standard enthalpy of formation (ΔH_f°) as a reference point.

1) The standard enthalpy of formation, ΔH_f° of any element in its most stable form is zero.

$$\Delta H_f^0 (\text{O}_2) = 0$$

$$\Delta H_f^0 (\text{O}_3) = 142 \text{ kJ/mol}$$

$$\Delta H_f^0 (\text{C, graphite}) = 0$$

$$\Delta H_f^0 (\text{C, diamond}) = 1.90 \text{ kJ/mol}$$

$$\Delta H_f^0 (\text{S}_8, \text{ rhombic}) = 0 \text{ kJ/mol}$$

The standard enthalpy of formation, ΔH_f° of many compounds is tabulated in many handbooks. This gives us predictive capability and is someone useful in the real world.

TABLE 6.4

Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.0	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.9
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(g)	81.56
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-271.6	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-348.0
H ₂ O(l)	-285.8		



Writing Formation Equations

Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include ΔH_f^0 .

- (a) Silver chloride, AgCl, a solid at standard conditions.
- (b) Calcium carbonate, CaCO₃, a solid at standard conditions.
- (c) Hydrogen sulfide, H₂S, a gas at standard conditions.

PLAN: *Use the table of heats of formation for values. Remember 1 mole of product is formed and fractions are allowed as coefficients.*



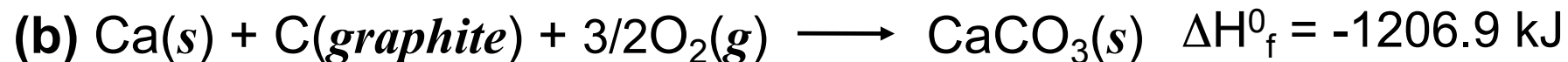
Writing Formation Equations

Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include ΔH_f^0 .

- (a) Silver chloride, AgCl, a solid at standard conditions.
- (b) Calcium carbonate, CaCO₃, a solid at standard conditions.
- (c) Hydrogen cyanide, HCN, a gas at standard conditions.

PLAN: Use the table of heats of formation for values.

SOLUTION:



Using heats of formation ΔH_f° , to determine enthalpies of reactions, ΔH_{rxn}° .

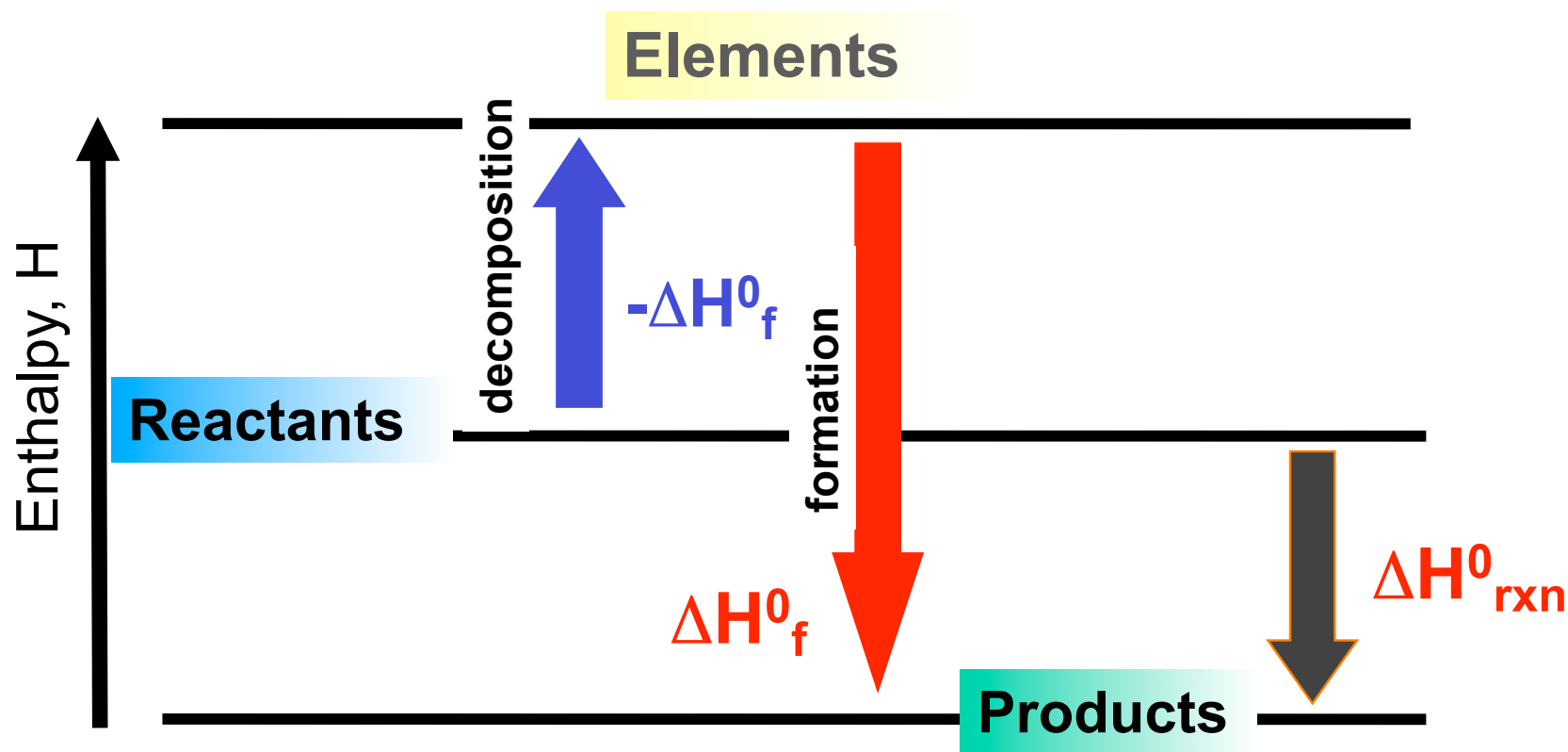
2-Problem Types To Expect For Enthalpy Calculations

Equations where each enthalpy data is provided and you use Hess's Law to calculate enthalpy of another reaction.

Use ΔH_f° data from a table and use the equation:

$$\Delta H_{rxn}^\circ = \sum n_i \Delta H_{if}^\circ(\text{products}) - \sum m_i \Delta H_{jf}^\circ(\text{reactants})$$

Energy level diagrams are useful pictorials of the thermodynamic transitions that take place during a chemical reaction.



$$\Delta H^{\circ}_{rxn} = \sum m \Delta H^{\circ}_{f(\text{products})} - \sum n \Delta H^{\circ}_{f(\text{reactants})}$$

The enthalpy of any reaction, $\Delta H^\circ_{\text{rxn}}$ can be obtained by using standard heats of formations and the following equation:

$$\Delta H^\circ_{\text{rxn}} = \sum n_i \Delta H_{i\text{f}}^\circ(\text{products}) - \sum m_i \Delta H_{j\text{f}}^\circ(\text{reactants})$$

where \sum means “the sum of”

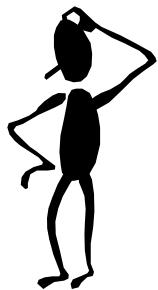
n_i is the respective stoich coefficient for i^{th} *product*

m_i is the respective stoich coefficient for each i^{th} *reactant*

Example: Suppose $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$ $\Delta H^\circ_{\text{rx}} = ?$

$$\Delta H^\circ_{\text{rx}} = \Delta H^\circ_{\text{f}}(\text{Products}) - \Delta H^\circ_{\text{f}}(\text{Reactants})$$

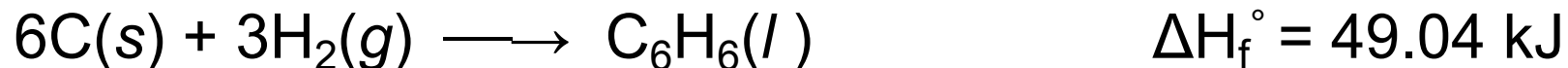
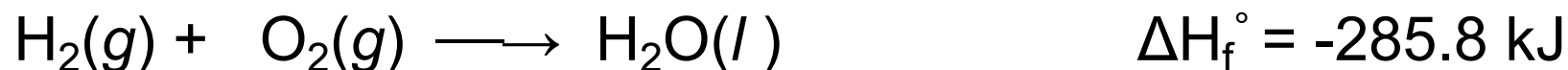
$$\Delta H^\circ_{\text{rx}} = [c\Delta H^\circ_{\text{f}}(\text{C}) + d\Delta H^\circ_{\text{f}}(\text{D})] - [a\Delta H^\circ_{\text{f}}(\text{A}) + b\Delta H^\circ_{\text{f}}(\text{B})]$$

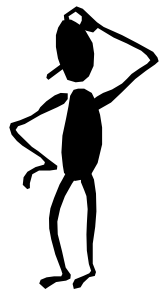


Calculating ΔH_f° from tabulated data

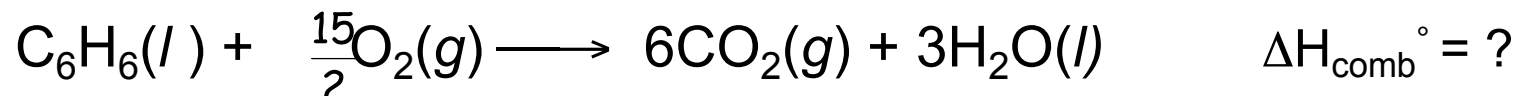
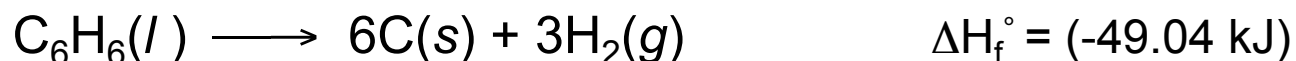
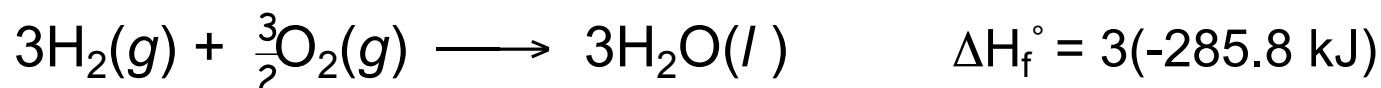
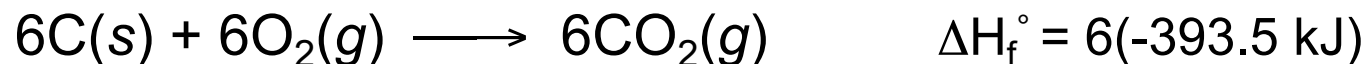
Calculate the ΔH_{comb} for the combustion of 2 moles of $\text{C}_6\text{H}_6(l)$ from enthalpies of formation data table.

ΔH_f° Data From Table In Back of the Textbook (or Handbook of Physics and Chemistry)





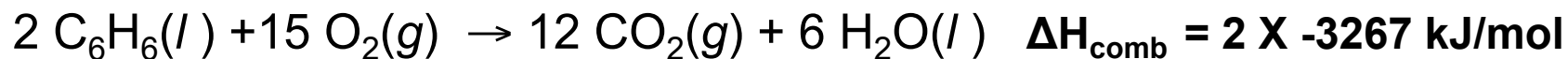
Calculating ΔH_f° from tabulated data

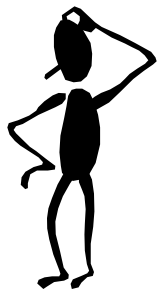


$$\Delta H_{\text{comb}}^\circ = [6(-393.5 \text{ kJ}) + 3(-285.8 \text{ kJ})] - [(-49.04 \text{ kJ})] = -3,267.4 \text{ kJ}$$

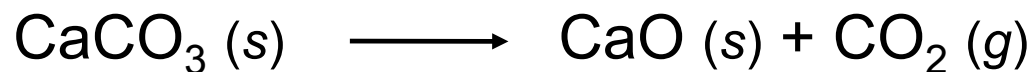
$$\Delta H_{\text{rxn}}^\circ = \sum n_i \Delta H_{if}^\circ(\text{products}) - \sum m_i \Delta H_{jf}^\circ(\text{reactants})$$

that's for one mole of benzene only!

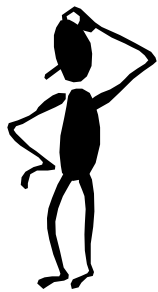




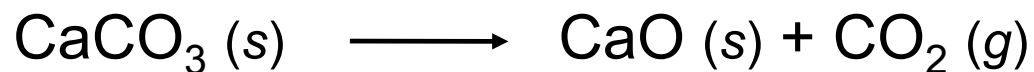
Calculate the heat of decomposition for the following process using standard enthalpies of formation found in Appendix. What kind of reaction is this? Is energy given off or needed to make this reaction proceed?



$$\Delta H^\circ_{\text{rxn}} = \sum n_j \Delta H_{if}^\circ(\text{products}) - \sum m_i \Delta H_{if}^\circ(\text{reactants})$$



Calculate the heat of decomposition for the following process using standard enthalpies of formation found in Appendix. What kind of reaction is this? Is energy given off or needed to make this reaction proceed?

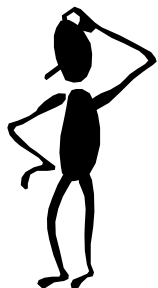


$$\Delta H^\circ_{\text{rxn}} = \sum n_i \Delta H_{i_f}^\circ(\text{products}) - \sum m_i \Delta H_{i_f}^\circ(\text{reactants})$$

$$\Delta H^\circ_{\text{rxn}} = [\Delta H_f^\circ(\text{CaO}) + \Delta H_f^\circ(\text{CO}_2)] - [\Delta H_f^\circ(\text{CaCO}_3)]$$

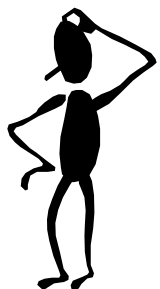
$$\Delta H^\circ_{\text{rxn}} = [-635.6 + -393.5] - [-1206.9] = 179 \text{ kJ}$$

Reaction is decomposition and endothermic. Energy must be absorbed to proceed.

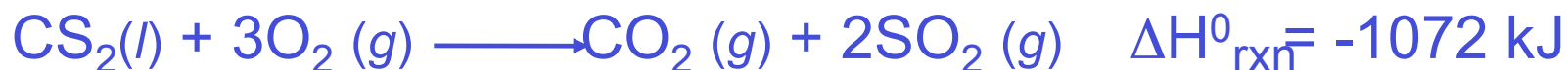


Calculate the standard enthalpy of formation of $\text{CS}_2(l)$ given that:





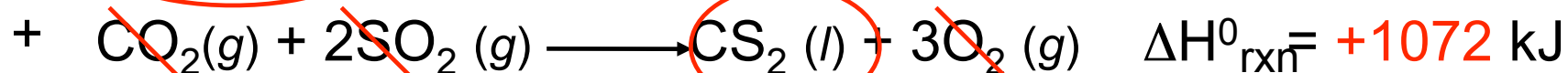
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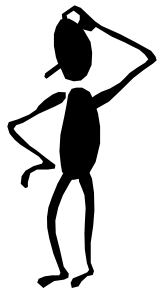
1. Write the enthalpy of formation reaction for CS_2



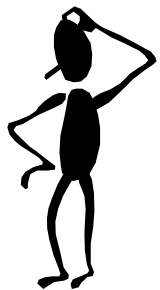
2. Add the given rxns so that the result is the desired rxn.



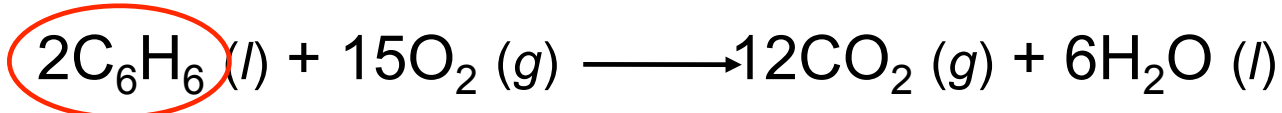
$$\Delta H^\circ_{\text{rxn}} = -393.5 + (2 \times -296.1) + 1072 = 86.3 \text{ kJ}$$



Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.



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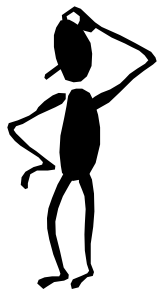


$$\Delta H_{\text{rxn}}^0 = \sum n\Delta H_f^0(\text{products}) - \sum m\Delta H_f^0(\text{reactants})$$

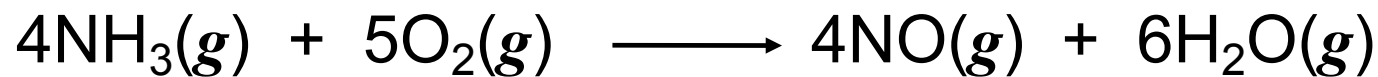
$$\Delta H_{\text{rxn}}^0 = [12\Delta H_f^0(CO_2) + 6\Delta H_f^0(H_2O)] - [2\Delta H_f^0(C_6H_6)]$$

$$\Delta H_{\text{rxn}}^0 = [12 \times -393.5 + 6 \times -285.8] - [2 \times 49.04] = -6534 \text{ kJ}$$

$$\frac{-6534 \text{ kJ}}{2 \text{ mol}} = -3267 \text{ kJ/mol } C_6H_6$$



Nitric acid, whose worldwide annual production is about 8 billion kilograms, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:



Calculate ΔH_{rxn}^0 from ΔH_{f}^0 values.

PLAN: *Look up the ΔH_{f}^0 values in Appendix and use Hess's Law to find ΔH_{rxn}^0 .*

$$\Delta H_{\text{f}}^0 \text{ NH}_3(g) = -46.3 \text{ kJ/mol}$$

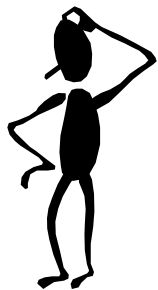
$$\Delta H_{\text{f}}^0 \text{ O}_2(g) = 0$$

$$\Delta H_{\text{f}}^0 \text{ H}_2\text{O}(g) = -241.8 \text{ kJ/mol}$$

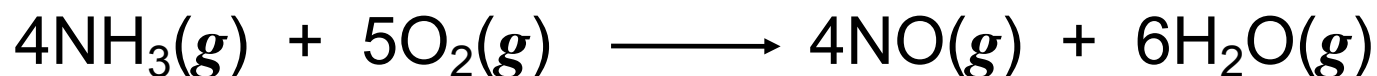
$$\Delta H_{\text{f}}^0 \text{ NO}(g) = 90.4 \text{ kJ/mol}$$

Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(<i>s</i>)	0	H ₂ O ₂ (<i>l</i>)	-187.6
AgCl(<i>s</i>)	-127.0	Hg(<i>l</i>)	0
Al(<i>s</i>)	0	I ₂ (<i>s</i>)	0
Al ₂ O ₃ (<i>s</i>)	-1669.8	HI(<i>g</i>)	25.9
Br ₂ (<i>l</i>)	0	Mg(<i>s</i>)	0
HBr(<i>g</i>)	-36.2	MgO(<i>s</i>)	-601.8
C(graphite)	0	MgCO ₃ (<i>s</i>)	-1112.9
C(diamond)	1.90	N ₂ (<i>g</i>)	0
CO(<i>g</i>)	-110.5	NH ₃ (<i>g</i>)	-46.3
CO ₂ (<i>g</i>)	-393.5	NO(<i>g</i>)	90.4
Ca(<i>s</i>)	0	NO ₂ (<i>g</i>)	33.85
CaO(<i>s</i>)	-635.6	N ₂ O ₄ (<i>g</i>)	9.66
CaCO ₃ (<i>s</i>)	-1206.9	N ₂ O(<i>g</i>)	81.56
Cl ₂ (<i>g</i>)	0	O(<i>g</i>)	249.4
HCl(<i>g</i>)	-92.3	O ₂ (<i>g</i>)	0
Cu(<i>s</i>)	0	O ₃ (<i>g</i>)	142.2
CuO(<i>s</i>)	-155.2	S(rhombic)	0
F ₂ (<i>g</i>)	0	S(monoclinic)	0.30



Nitric acid, whose worldwide annual production is about 8 billion kilograms, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:



Calculate ΔH_{rxn}^0 from ΔH_{f}^0 values.

SOLUTION: $\Delta H_{\text{rxn}} = \sum m\Delta H_{\text{f}}^0$ (products) - $\sum n\Delta H_{\text{f}}^0$ (reactants)

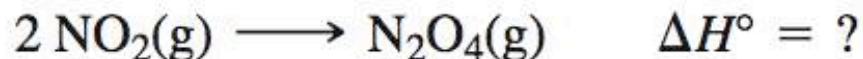
$$\Delta H_{\text{rxn}} = [4(\Delta H_{\text{f}}^0 \text{NO}(\text{g})) + 6(\Delta H_{\text{f}}^0 \text{H}_2\text{O}(\text{g}))] - [4(\Delta H_{\text{f}}^0 \text{NH}_3(\text{g})) + 5(\Delta H_{\text{f}}^0 \text{O}_2(\text{g}))]$$

$$= (4 \text{ mol})(90.4 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol}) -$$

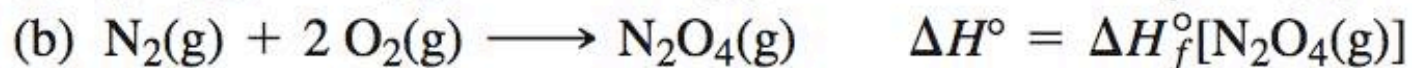
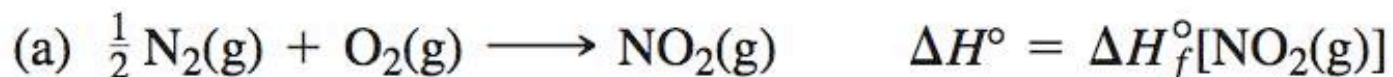
$$[(4 \text{ mol})(-46.3 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = -904 \text{ kJ}$$

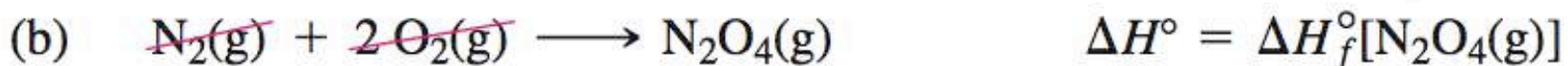
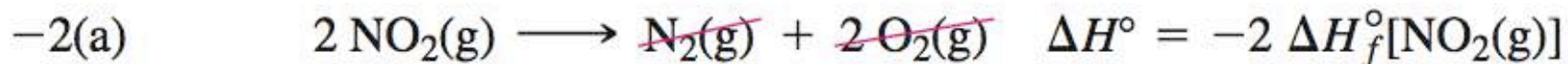
Heats of Reaction From ΔH_f°



The standard enthalpies of formation of these two gases can be found in Table 6.2:



With Hess's law, we can combine these two equations and arrive at the equation we want. To do this, we first reverse and then double equation (a):



$$\Delta H^\circ = \Delta H_f^\circ[\text{N}_2\text{O}_4(\text{g})] - 2 \times \Delta H_f^\circ[\text{NO}_2(\text{g})]$$